



Eur päisches Patentamt
Eur pean Patent Offic
Offic europé n des brevets



⑪ Publication number:

0 518 653 B1

⑫

EUROPEAN PATENT SPECIFICATION

④⑤ Date of publication of patent specification: 06.09.95 ⑤① Int. Cl.⁸: D06L 1/02

②① Application number: 92305338.3

②② Date of filing: 11.06.92

The file contains technical information submitted
after the application was filed and not included in
this specification

⑤④ Method and composition using densified carbon dioxide and cleaning adjunct to clean fabrics.

③① Priority: 14.06.91 US 715299

④③ Date of publication of application:
16.12.92 Bulletin 92/51

④⑤ Publication of the grant of the patent:
06.09.95 Bulletin 95/36

⑥④ Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU MC
NL PT SE

⑤⑥ References cited:
DE-A- 2 027 003
DE-A- 3 904 514
DE-A- 4 004 111
US-A- 4 012 194
US-A- 4 219 333

⑦③ Proprietor: The Clorox Company
1221 Broadway
Oakland
California 94612 (US)

⑦② Inventor: Mitchell, James D.
1694 Cervato Circle
Alamo,
California 94507 (US)
Inventor: Carty, Daniel T.
50 Tyrrel Court
Danville,
California 94526 (US)
Inventor: Latham, James R.
1798 Warsaw Street
Livermore,
California 94550 (US)

⑦④ Representative: Smith, Sydney et al
Elkington and Fife
Prospect House
8 Pembroke Road
Sevenoaks, Kent TN13 1XR (GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

EP 0 518 653 B1

Description**1. Field of the Invention**

5 The invention provides a method for the removal of especially nonpolar stains from fabrics by using a densified carbon dioxide and a cleaning adjunct, which is a nonpolar liquid.

2. Brief Statement on Related Art

10 There has been limited recognition in the use of carbon dioxide to clean fabrics. Carbon dioxide has been used a standard propellant in the delivery of foaming cleaning products, e.g., Harris, U.S. Pat. No. 4,219,333.

Maffei, U.S. Pat. No. 4,012,194, described a dry cleaning system in which chilled liquid carbon dioxide is used to extract soils adhered to garments. The liquid carbon dioxide is converted to gaseous carbon dioxide, the soils removed in an evaporator and the gaseous carbon dioxide is then recycled. Maffei, however, does not teach, disclose or suggest the use of additional cleaning adjuncts in connection with his chilled liquid carbon dioxide dry cleaning system.

15 More recently, the use of supercritical fluids, e.g., carbon dioxide whose temperature has been elevated to past a so-called critical point, has been studied for the purposes of solvent extraction, as in, e.g., Kirk-Othmer, Encycl. of Chem. Tech., 3d Ed., Vol. 24 (Supplement), pp. 872-893 (1983) and Brogle, "CO₂ in Solvent Extraction," Chem. and Ind., pp. 385-390 (1982). This technology is of high interest because of the need for little or no organic solvents in such extraction processes, which is very desirable from an environmental standpoint.

20 In DE-A-4,004,111 there is described a process for the pretreatment of textile surfaces for the removal of fibre-associated materials with a fluid in which the fluid is a supercritical fluid. A moderator such as water may be added to the supercritical liquid. This may contain paraffin hydrocarbons.

In DE-A-2,027,003 there is described a process for the cleaning of articles contaminated with oil in which the contaminated article is contacted with a petroleum mineral oil and the excess oil removed.

25 However, none of the prior art discloses, teaches or suggests the combination of densified carbon dioxide and a cleaning adjunct as a cleaning agent for the removal of soils and stains from fabrics, said cleaning adjunct being a nonpolar liquid. Nor does the art teach, disclose or suggest the use of such combination of densified carbon dioxide and a cleaning adjunct in a dry cleaning process, the novel combination providing an environmentally safe alternative to the use of ordinary dry cleaning materials such as Stoddard solvent or perchloroethylene ("perc").

SUMMARY OF THE INVENTION AND OBJECTS

35 The invention provides a method for the removal of nonpolar stains from a fabric comprising:

contacting said stains first with a nonpolar cleaning adjunct with a viscosity of 0.5 MPa.s (0.5 cps) or greater at standard temperature and pressure and thereafter with a fluid medium which is either densified or supercritical carbon dioxide.

40 By the method of the invention an improved method for the dry cleaning of fabrics is provided which avoids significant use of such solvents as perchloroethylene and Stoddard solvent, or similar hydrocarbon solvents.

45 The combined densified carbon dioxide/adjunct system according to the invention has surprisingly superior performance over the use of either carbon dioxide or adjunct alone applied to the stain.

The method of the invention to remove nonpolar soils from fabrics avoids the use of water and other solvents which could, upon removal from the fabric, cause damage to the fabric by shrinkage or warping.

BRIEF DESCRIPTION OF THE DRAWINGS

50 Fig. 1 is a schematic of a preferred embodiment of the invention, namely, a dry cleaning operation.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

55 As indicated the invention provides a method for removing nonpolar stains from fabrics utilizing a cleaning adjunct having a viscosity of at least 0.5 MPa.s (0.5 cps) and densified or supercritical carbon dioxide.

A particularly preferred application of the invention is in the use of the cleaning method for the nonaqueous cleaning of stained fabrics commonly known as dry cleaning.

Dry cleaning is conducted primarily by small businesses, many of which have been in operation for many years prior to the onset of stringent environmental legislation regarding the use and disposal of organic solvents, e.g., perc and Stoddard solvent. Because of the ever-growing concern that ground waters may become contaminated by the widescale use of such solvents, much of this new legislation has been promulgated to regulate such use and disposal. Consequently, there is a great need for alternate ways of cleaning fabrics avoiding the use of such solvents, while obtaining effective cleaning for garments and other fabrics for which aqueous washing is contraindicated.

In the present invention, numerous definitions are utilized:

"Densified carbon dioxide" means carbon dioxide, normally a gas, placed under pressures generally exceeding preferably 5,516 kPa (800 psi) at standard temperature (21 °C).

"Nonpolar cleaning adjuncts" refer to nonpolar materials which are typically liquids at room temperature (21 °C) and preferably, have a viscosity of 0.5 mPa.s (centipoise) ("cps") or greater. They are not necessarily solvents or cleaners in the classic sense, but in the invention, function to remove soils from fabrics. They are preferably selected from substituted and unsubstituted hydrocarbons, in particular a C₅₋₂₄ paraffin, such as mineral oil or petrolatum.

"Nonpolar stains" are those which are at least partially made by nonpolar organic compounds, such as hydrocarbon compounds (petroleum based products, such as motor oil), and other compounds typically considered to form oily soils, e.g.s., without limitation, carboxylic acids (fatty acids), glycerides, sebum and the like.

"Supercritical" phase means when a substance, such as carbon dioxide, exceeds a critical temperature (e.g., 31 °C), at which point the material cannot be condensed into the liquid phase despite the addition of further pressure.

1. Densified carbon dioxide

Carbon dioxide (CO₂) is a colorless gas which can be recovered from coal gasification, synthetic ammonia and hydrogen generation, fermentation and other industrial processes. (Kirk-Othmer, Encycl. Chem. Tech., 3rd Ed., Vol. 4, pp. 725-742 (1978).

In the invention, densified carbon dioxide is used as a solvent for removing soils and stains from fabrics, in conjunction with the viscous cleaning adjunct. Densified carbon dioxide, as defined above, is carbon dioxide which has been placed under greater than atmospheric pressure or low temperature to enhance its density. In contrast to carbon dioxide used in pressurized canisters to deliver foamed products, e.g., fire extinguishers or shaving creams, densified carbon dioxide is preferably at much greater pressures, e.g., 5,516 kPa (800 p.s.i.) and greater. It has been found that density, rather than temperature or pressure alone, has much greater significance for enhancing the solvent-like properties of carbon dioxide. See, H. Brogle, "CO₂ as a Solvent: its Properties and Applications," Chem. and Ind., pp. 385-390 (1982).

Types of densified carbon dioxide which would be of utility herein includes densified carbon dioxide and supercritical carbon dioxide.

The amount, or volume, of densified or supercritical carbon dioxide depends on the type of substrate, temperature and pressure involved. Generally, an amount which is effective to remove the stain is used. Thus, for the purposes of this invention, cleaning-effective amounts are used.

2. Viscous Cleaning Adjunct

By itself, densified carbon dioxide has relatively poor soil removal performance. Surprisingly, applicants have discovered that the addition of a relatively viscous cleaning adjunct, generally speaking, an organic compound, can unexpectedly improve the removal of oily soils, particularly, hydrocarbon-based soils, from fabrics soiled with such oily soils. This is all the more surprising considering that such cleaning adjuncts themselves are not very effective at removing such oily soils from fabrics in the absence of densified carbon dioxide.

The cleaning adjuncts used herein are generally, nonpolar organic chemicals. As mentioned above, the adjuncts have a viscosity of at least about .5 mPa.s (.5 centipoise) at standard temperature. Nonpolar compounds useful herein include substituted and unsubstituted hydrocarbons.

Preferred cleaning adjuncts are the C₅₋₂₄ alkanes. These may be n-, s-, unsubstituted, substituted, cyclo-, branched and mixtures thereof. Especially preferred are paraffin oils, which have a mixture of alkanes and include some portion of C₁₆ and higher hydrocarbon content. Examples include mineral oil and

TABLE I

Cleaning Agent	Adjusted % Stain Removal	Std. Dev. (+/-)
Dens CO ₂	38.0	2.2
Paraffin Oil	0.0	3.9
Dense CO ₂ /Paraffin Oil	55.5	4.0

The foregoing results demonstrate the unexpected superiority of the inventive cleaning composition and method over the use of dense CO₂ and a cleaning adjunct used singly. The cleaning improvement was much more than merely additive, thus proving a true showing of synergism between the components of the inventive cleaner.

Claims

1. A method for the removal of nonpolar stains from a fabric comprising:
contacting said stains first with a nonpolar cleaning adjunct with a viscosity of 0.5 MPa.s (0.5 cps) or greater at standard temperature and pressure and thereafter with a fluid medium which is either densified or supercritical carbon dioxide.
2. The method of claim 1 further comprising the step of removing the mixture of the nonpolar cleaning adjunct and the densified or supercritical carbon dioxide and said stains.
3. A method as claimed in claim 1 or claim 2 characterized in that the densified carbon dioxide has a pressure, at room temperature, of greater than 800 psi (55 Bar).
4. A method as claimed in any of claims 1-3 characterized in that the cleaning adjunct is selected from substituted and unsubstituted hydrocarbons and mixtures thereof.
5. A method as claimed in any of claims 1 to 4 characterized in that the cleaning adjunct is a C₅-24 paraffin.
6. A method as claimed in claim 5 characterized in that the paraffin is mineral oil.
7. A method as claimed in claim 5 characterized in that the paraffin is petrolatum.

Patentansprüche

1. Verfahren zur Entfernung von nichtpolarem Schmutz aus einem textilen Flächengebilde, gemäß dem der Schmutz zuerst mit einem nichtpolaren Reinigungszusatzmittel mit einer Viskosität von 0,5 MPa.s (0,5 cps) oder größer bei Standardtemperatur und -druck und anschließend mit einem fluiden Medium, welches entweder verdichtetes oder superkritisches Kohlendioxid ist, behandelt wird.
2. Verfahren nach Anspruch 1, welches weiter die Stufe der Entfernung des Gemisches aus nichtpolarem Reinigungszusatzmittel und verdichtetem oder superkritischem Kohlendioxid und dem Schmutz umfaßt.
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das verdichtete Kohlendioxid einen Druck bei Raumtemperatur von über 800 psi (55 bar) besitzt.
4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das Reinigungszusatzmittel ausgewählt wird aus substituierten und unsubstituierten Kohlenwasserstoffen und den Gemischen davon.
5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das Reinigungszusatzmittel ein C₅-24-Paraffin ist.
6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß das Paraffin Mineralöl ist.

petrolatum.

Referring particularly to hydrocarbon cleaning adjuncts, it has been found that when paraffins are used as the cleaning adjunct with densified carbon dioxide, and the first precedes the second especially enhanced cleaning, beyond that expected by the combination thereof, is achieved against a nonpolar stain (dirty motor oil). This synergistic cleaning action was unexpected and evidences the superior performance of the cleaning method hereunder.

It is also important to recognize that the cleaning adjunct is not a part of the homogeneous, densified or supercritical fluid system. Instead, the cleaning adjunct is added to the fabric to be cleaned prior to the application of the densified fluid, forming a heterogeneous cleaning system. Thus, the use of these cleaning adjuncts is readily distinguishable from prior art systems, in which entrainers, or co-gassifiable substances form part of the densified or supercritical fluid matrix.

The amount, or volume of the cleaning adjunct similarly varies, but is most preferably a soil-solubilizing or -removing amount. The precise mechanism for soil removal in this invention is not completely understood and thus, precise characterization of the amount of the adjunct is not presently available. However, generally speaking, although nonpolar cleaning adjuncts were found not effective at removing nonpolar soils from fabrics by themselves, in conjunction with the densified carbon dioxide, unexpectedly effective cleaning was achieved.

In the practice of the best mode of this invention, reference is conveniently made to the drawing, Fig. 1, which is a schematic depiction of the dry cleaning process and equipment suited thereto.

In Fig. 1 is generally depicted the dry cleaning operation. A pressurized gas cylinder 8 contains densified CO₂, whose outflow can be regulated by in-line valve 4A. The gas cylinder is connected by means of tubing to pump 10, e.g., an electrically driven LDC pump, which pressurizes the CO₂ along with regulator 12. A further valve 4B passes densified CO₂ to be read by pressure gauge 14. The densified CO₂ is fed into autoclave 18, in which the soiled fabrics are placed. The temperature of the densified CO₂ is controlled by passing the CO₂ through a heat exchange coil 16 located in autoclave 18. The temperature is measured by a digital thermometer 20 connected to a thermocouple (not shown). The densified CO₂ and soil is then passed through valve 4C which is in line with heated control valve 6, which controls the extraction rate. Further downstream, an expansion vessel 22 collects the extracted soils, while flow gauge 24 measures the rate of extraction. The gas meter 26 measures the volume of CO₂ used.

Using the operation outlined above, extractions of oily soils were undertaken using a preferred embodiment of the invention, in which the stained fabric was contacted with paraffin oil (about C₁₈ alkane) for about 15 minutes and then treated with dense CO₂. This was compared against the extraction by dense CO₂ and paraffin oil singly.

EXPERIMENTAL

Several cotton swatches (Testfabric Inc. #400) were uniformly stained with dirty motor oil drained from an automobile crankcase. The swatches were allowed to set for an appropriate amount of time (aged about one week). Three sets of swatches were run in triplicate and were contacted with 1) paraffin oil only, as a solvent treatment; 2) dense CO₂ only; and 3) a combination of dense CO₂ and paraffin oil.

In the treatment with paraffin oil only, Baker paraffin oil with a viscosity of about 350 mPa.s (350 cps) at about 37.7°C, was applied to the dirty swatch, was allowed to soak in and dried for 15 minutes. The amount of oil used was about 1 gram per swatch (also 1g).

In the latter two treatments, the swatches were placed in the reaction chamber (autoclave) and CO₂ (about 5,516 kPa (800 psi), 20°C) was applied as described above. In treatment 2), the swatch were contacted with CO₂ as described. In treatment 3), the inventive treatment, the swatch was first contacted with 1g of paraffin oil and allowed to set for 15 minutes. The mass of CO₂ used was about 1750 g CO₂ (the volume will depend on temperature and pressure used) and time of treatment varied. The relative solubility of the adjunct is significant in determining the amount of CO₂ to use versus amount of adjunct. In the case of paraffin oil, it was determined that about 1,800: 1 weight ratio was optimal.

The results are shown below:

7. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß das Paraffin Petrolatum ist.

Revendications

- 5 1. Procédé pour l'élimination des taches non polaires d'un tissu, comprenant :
le contact desdites taches d'abord avec un additif de nettoyage non polaire ayant une viscosité de 0,5 MPa.s (0,5 cP) ou plus à la température et à la pression standard, puis avec un milieu fluide qui est du dioxyde de carbone soit densifié soit supercritique.
- 10 2. Procédé selon la revendication 1, comprenant de plus l'étape d'élimination du mélange de l'additif de nettoyage non polaire et du dioxyde de carbone densifié ou supercritique et desdites taches.
3. Procédé selon la revendication 1 ou la revendication 2, caractérisé en ce que le dioxyde de carbone densifié a une pression, à la température ordinaire, supérieure à 800 psi (55 bars).
- 15 4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que l'additif de nettoyage est choisi parmi les hydrocarbures substitués et non substitués et leurs mélanges.
5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que l'additif de nettoyage
20 est une paraffine en C₅₋₂₄.
6. Procédé selon la revendication 5, caractérisé en ce que la paraffine est une huile minérale.
7. Procédé selon la revendication 5, caractérisé en ce que la paraffine est la vaseline.

25

30

35

40

45

50

55

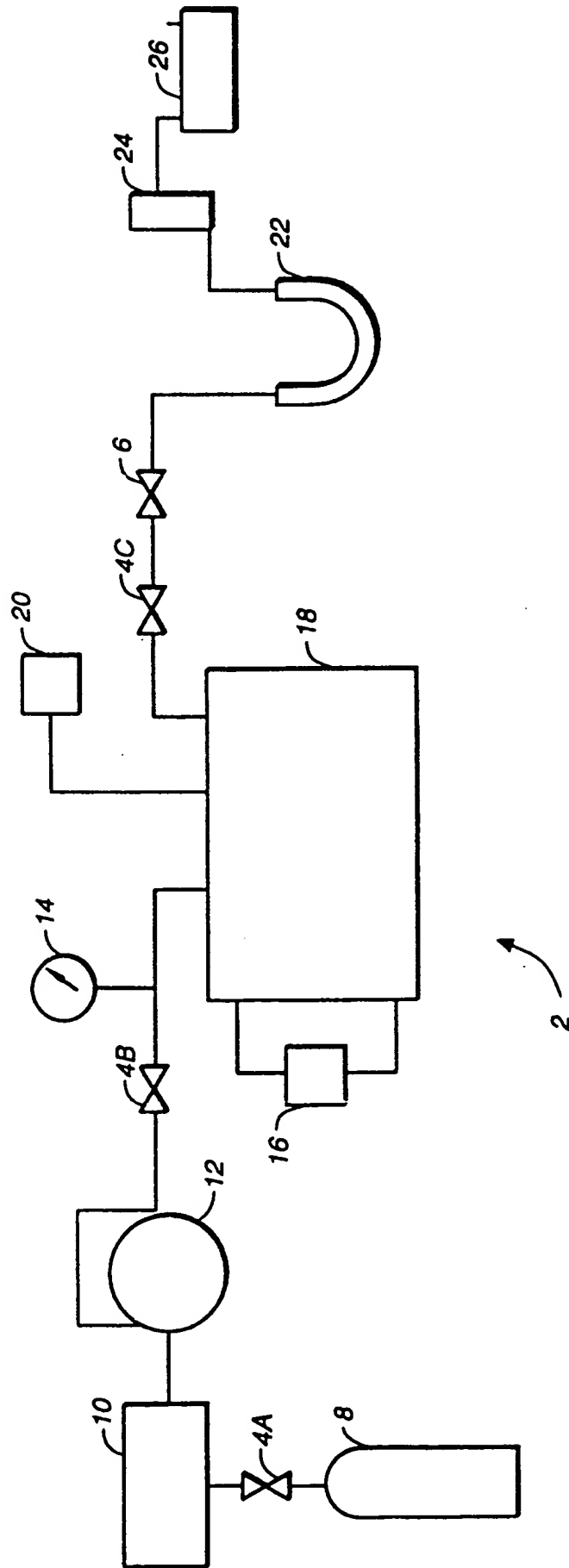


FIG. 1